



Adsorption of Cr(VI) using silica-based adsorbent prepared by radiation-induced grafting

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ABSTRACT

Silica-based adsorbent was prepared by radiation-induced grafting of dimethylaminoethyl methacrylate (DMAEMA) onto the silanized silica followed by a protonation process. The FTIR spectra and XPS analysis proved that DMAEMA was grafted successfully onto the silica surface. The resultant adsorbent manifested a high ion exchange capacity (IEC) of ca. 1.30 mmol/g and the Cr(VI) adsorption behavior of the adsorbent was further investigated, revealing the recovery of Cr(VI) increased with the adsorbent feed and the equilibrium adsorption could be achieved within 40 min. The adsorption capacity, strongly depended on the pH of the solution, reached a maximum Cr(VI) uptake (ca. 68 mg/g) as the pH was in the range of 2.5–5.0. Furthermore, even in strong acidic (4.0 mol/L HNO₃) or alkaline media (pH 11.0), the adsorbent had a sound Cr(VI) uptake capacity (ca. 22 and 30 mg/g, respectively), and the adsorption followed Langmuir mode. The results indicated that this adsorbent, prepared via a convenient approach, is applicable for removing heavy-metal-ion pollutants (e.g. Cr(VI)) from waste waters.

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1. Introduction

The environmental pollution problem such as releasing industrial waste waters into rivers directly has been attracting more and more attention during the past few decades, and the most serious pollutants are heavy metal ions that mostly coming from industrial waters. These heavy metal ions could not only lead to direct and indirect health risk of human beings but also disserve the whole ecosystem, as a result the removal of those toxic substance from industrial effluents has been becoming an urgent issue. By far many kinds of treatment techniques have been employed to solve this problem, for instance ion-exchange, reverse osmosis, precipitation, filtration, coagulation, electrolytic recovery and so on [1–7]. Such techniques, however, have many disadvantages that include high chemical cost, low removal efficiency, high-energy requirement and the generation of secondary toxic slurries. Compounds con-

taining toxic elements like chromium (Cr) are widely used in a great number of modern industries such as leather tanning, electroplating, metal finishing and pigments production, which result in a large quantity of Cr(VI) ions discharged directly into industrial waste effluent. Researches [8–10] have indicated that the Cr(VI) ions can bring high toxic nature to the biological systems and human health: Inhalation of Cr(VI) may cause acute toxicity, irritation and ulceration of the nasal septum and respiratory sensitization (asthma); Ingestion of Cr(VI) may affect kidney and liver functions; Skin contact with Cr(VI) may result in systemic poisoning damage or even severe burns, and interference with the healing of cuts or scrapes, which may lead to ulceration and severe chronic allergic contact dermatitis; Eye exposure to Cr(VI) may cause permanent damage. Environmental Protection Agency (EPA) in US recommends that the amount of Cr(VI) in drinking water should be less than 100 µg/L. Due to its high toxic nature to biological systems, the removal of Cr(VI) from these liquid waste has attracted a mass of public's concern. In order to develop a proper method for the removal of Cr(VI) from industrial effluents, many adsorbents have been exploited, such as activated clay [11], ion exchange resin [12], activated carbon [13], natural rectorite [14], and zeolite [15].

Radiation grafting technique has been widely used to prepare adsorbents for removing the heavy metal ions from effluents in the past several decades [7,16–19] and the process can be carried out at room temperature. Plenty of functional materials

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were prepared by choosing different functional monomers and matrix materials freely. What's more, the adsorbents with different grafting yield (*GY*) can be easily prepared by controlling the irradiation conditions. Dimethylaminoethyl methacrylate (DMAEMA) has been grafted onto various matrix materials by radiation technique [20–24]. As tertiary and quaternary amino groups can be easily incorporated into matrix materials, the DMAEMA grafted materials have also been utilized for adsorption and separation of heavy metal ions [21,22,25]. Moreover, the hydrogels prepared by radiation crosslinking of DMAEMA has displayed a sound ability to adsorb metal ions like ReO_4^- [26].

Owing to its high surface area, fast adsorption kinetics and chemical stability under acidic conditions, silica has been extensively used as porous matrix to prepare adsorbents for heavy-metal-ions like Cr(VI) [27–32]. Being capable of immobilizing various organic molecules onto the surface, silica is usually organofunctionalized with chelation groups providing the scopes for trapping heavy metal ions. Several kinds of silica-based adsorbents for Cr(VI) have been prepared in the past few years [28,33–35]. However, the application of those resultant adsorbents was largely limited due to their poor stability under particular circumstance such as in strong acidic solutions. Whereas the organofunctionalized methods usually involved complicated procedures, inducing to high cost, low reaction efficiency etc, it was necessary to explore novel methods for preparing silica-based adsorbent. Recently, some vinyl monomers have been grafted onto silica with irradiation method, confirming the feasibility of preparing adsorbents via radiation-induced grafting of monomers onto silica matrix [36,37].

In this study, a tertiary-ammonium-type silica-based adsorbent for Cr(VI) adsorption was synthesized by radiation-induced grafting. The properties concerning the Cr(VI) adsorption such as adsorption kinetics and the befitting pH, especially their possibility to be utilized in extreme environments (e.g. strong acidic conditions and irradiation fields), were to be investigated.

2. Experimental

2.1. Materials

Silica was purchased from Qingdao Meigao Co. Ltd. DMAEMA (Acros) with purity of 99% was used as the monomer. Trimethylchlorosilane of chemical purity was supplied by Sinopharm Chemical Regent Co. Ltd. Other chemicals used were analytical reagent (AR).

2.2. Preparation of the adsorbent

The silica was first heated at 200 °C and then washed with 1.0 mol/L HNO_3 at about 100 °C. After dried in vacuum at 80 °C, the silica was silanized with trimethylchlorosilane at 110 °C in xylene for 8 h. The silanized silica was immersed in a 1.0 mol/L DMAEMA solution. After getting rid of oxygen by nitrogen flow, the samples were irradiated to desired absorbed dose by γ -ray at room temperature with a dose rate of 41.5 Gy/min. The DMAEMA grafted silica was washed with acetone in a Soxhlet's extraction device to remove residues and then dried in vacuum at 80 °C.

The DMAEMA grafted silica was immersed in 1.0 mol/L HCl to prepare the adsorbent via a protonation process (shown in Fig. 1), and then the adsorbent was washed with deionized water to remove the residue HCl. Finally, it was dried in vacuum and kept for further use.

The grafting yield (*GY*) of the samples was determined by thermogravimetric analysis in a Q600 SDT instrument (USA). The measurements were performed, with a nitrogen flow rate of

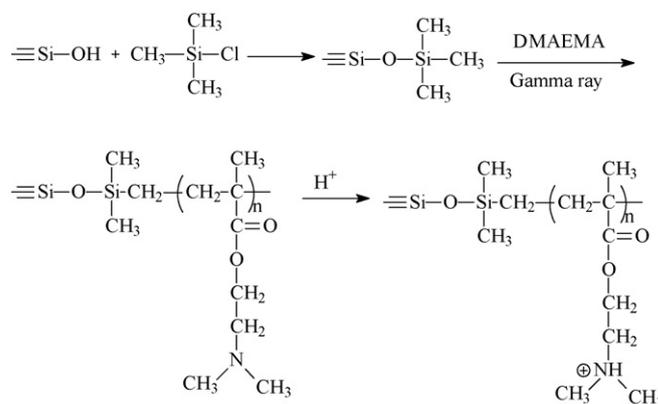


Fig. 1. Scheme of the synthesis route of the adsorbent.

100 mL/min, from room temperature to 1000 °C at a heating rate of 20 °C/min. According to the weight loss of the grafted silica due to the decomposition of the grafted DMAEMA, the *GY* was calculated as follows:

$$GY (\%) = \frac{W_g}{1 - W_g} \times 100 \quad (1)$$

where W_g is the weight loss percentage of the grafted silica due to the decomposition of the grafted DMAEMA.

2.3. Characterization of the adsorbent

Micro-FTIR analyses of the original silica, silanized silica and DMAEMA grafted silica was performed in a Nicolet (Magna-IR 750) spectrometer. The spectra were measured in the absorbance mode at a wave number range of 4000–600 cm^{-1} .

The ion exchange capacity (*IEC*) was determined by titration. The grafted silica with certain weight was immersed in a 0.05 mol/L HCl solution overnight at room temperature with periodic stirring. Then the solution was back titrated with 0.05 mol/L NaOH to neutral. The *IEC* (mmol/g) was calculated according to the following equation:

$$IEC = \frac{M_{\text{HCl}} - M_{\text{NaOH}}}{W} \quad (2)$$

where M_{HCl} is the initial mole of HCl, M_{NaOH} is that of the required NaOH, W is the weight of the grafted silica.

The X-ray photoelectron spectroscopy (XPS) analysis was performed with an AXIS-Ultra instrument from Kratos Analytical using monochromatic Al K α radiation (225 W, 15 mA, 15 kV) and low-energy electron flooding for charge compensation. To compensate for surface charges effects, binding energies were calibrated using C 1s hydrocarbon peak at a binding energy (BE) of 284.80 eV. The data were converted into VAMAS file format and imported into CASA XPS software package for manipulation and curve fitting.

2.4. Adsorption of Cr(VI) using the adsorbent

The stock Cr(VI) solution was prepared by dissolving $\text{K}_2\text{Cr}_2\text{O}_7$ in distilled water. Certain amount of HCl was added to stabilize Cr(VI) ions in the solution. After diluted to a total volume of 1.0 L, a stock solution with a Cr(VI) concentration of 1000 mg/L and HCl concentration of 0.02 mg/L was prepared. For the adsorption experiment, the Cr(VI) was determined using the Atom Emission Absorption Spectra (Hitachi, mode 180-60). The Cr(VI) uptake was calculated as

$$\text{Cr(VI) uptake} = \frac{(C_0 - C_e) \times V}{m} \quad (3)$$

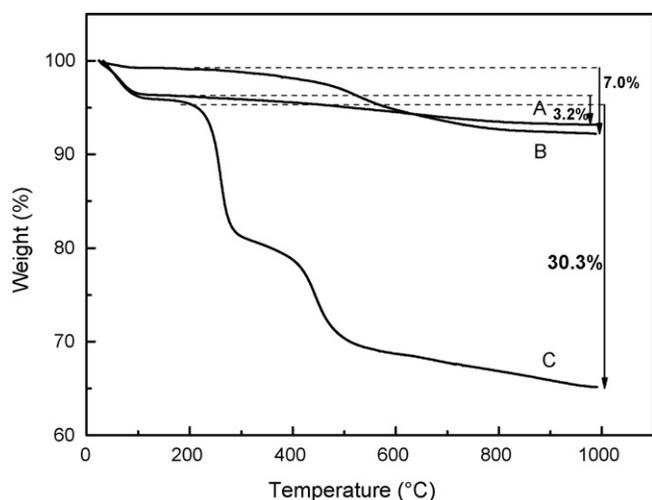


Fig. 2. TGA spectra of the original silica (A), silanized silica (B) and DMAEMA grafted silica (C).

where C_0 and C_e are the concentration of Cr(VI) before and after the adsorption, respectively; V is the volume of the Cr(VI) solution and m is the weight of the adsorbent.

The kinetics study was performed in a 50 mL 100 mg/L solution at a constant pH of 5.0. The adsorbent feed was 1.0 g/L.

In order to study the effect of pH on the adsorption of Cr(VI), a series of 50 mL Cr(VI) solutions were adjusted with HCl or NaOH, then 50 mg adsorbent was added to the solution. After stirring for 2 h, the concentration of Cr(VI) in the solution was measured.

For the adsorption isotherm study, 50 mL Cr(VI) solutions with the different concentration ranging from 50 to 250 mg/L were used. The pH was kept at 5.0 while the adsorbent feed was 1.0 g/L.

3. Results and discussions

3.1. Preparation and characteristics of the adsorbent

The preparation of the silica-based adsorbent involves the following three steps: (1) the silica was silanized with trimethylchlorosilane; (2) DMAEMA was grafted onto the silanized silica through γ -ray radiation grafting technique; (3) the resultant DMAEMA grafted silica was then protonated in hydrochloric acid to obtain the adsorbent. The adsorbent was then characterized by TGA, FTIR and XPS.

3.1.1. TGA measurements

Thermogravimetric analysis is a convincing method to determine the relative amount of functional groups which have been introduced by silanizing and grafting onto the silica matrix. The TG spectra of the samples are shown in Fig. 2. The weight loss of the samples before 200 °C was attributed to the loss of water, while that between 200 and 1000 °C was due to the decomposition of the samples. The weight loss of original silica between 200 and 1000 °C was

around 3.2%, however, after silanized with trimethylchlorosilane, the weight loss reached approximately 7.0%. The result indicated that approximately 3.8% of the weight loss was attributed to the silanization of the silica. In the case of the DMAEMA grafted silica, the weight loss increased to 30.3%. The increment of the weight loss was credited to the decomposition of the grafted DMAEMA. Moreover, the two steps' weight loss with onset at 260 °C and at 440 °C were contributed to the loss of the $-\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ fragments and the decomposition of the graft chains, respectively [38]. Accordingly, from the TGA results, it was concluded that DMAEMA had been successfully grafted onto the silica. At a dose of 60 kGy, the GY of DMAEMA onto the silica could reach to 28.2%, which is rather high when compared with other works related to the introduction of functional groups onto silica. Tsuchida et al. [37] has investigated grafting of several vinyl monomers onto pre-irradiated silica and found that at an absorbed dose of 50 kGy with a reaction time of 24 h at 50 °C, the GY of styrene, vinyl acetate, *N*-vinylcarbazole, methyl methacrylate onto silica were 0.3%, 13.5%, 13.7% and 0.6%, respectively, which were much lower than that of DMAEMA grafted silica in this work. The high GY in this work could be owed to the silanization process of the silica before irradiation, which brought on the generation of more $-\text{CH}_2^*$ radicals on the silica surface.

According to the properties of the adsorbents prepared at different conditions listed in Table 1, it can be seen that the GY of the adsorbent strongly depends on the surface area of the original silica. Higher surface area leads to higher yield of the radicals on the surface under irradiation circumstance; therefore much higher GY could be obtained. Furthermore, the GY also increased with the absorbed dose caused by the increasing of radical amount.

3.1.2. FTIR spectra

The FTIR spectra of the samples are presented in Fig. 3. As shown in Fig. 3, the obvious absorption bands were ascribed to OH (3450 cm^{-1}), H_2O (1630 cm^{-1}), Si–O–Si (ν_s 1100 cm^{-1} , ν_{as} 807 cm^{-1}), Si–OH (ν_s 950 cm^{-1}) (where ν_s and ν_{as} refer to the symmetric and asymmetric stretching, respectively). The strong absorption bands of OH and H_2O indicated that large number of OH groups and H_2O existed on the surface of the silica [39]. After silanized with trimethylchlorosilane, absorption bands at 2960 cm^{-1} could be observed as a result of the stretch vibration of C–H in trimethylchlorosilane, which suggested the success of the silanization. For DMAEMA grafted silica, the absorption band at 1730 cm^{-1} was ascribed to the stretching vibration of the carboxyl group in DMAEMA, manifesting that DMAEMA has been grafted onto the silanized silica. The spectrum of the adsorbent was the same as that of the grafted silica.

3.1.3. XPS analysis

The XPS spectra of the samples are displayed in Fig. 4. Fig. 4(A) shows the Si 1s core-level spectrum of the original silica. Attributing to the Si–O₂ species, Si 1s spectrum could be curve-fitted with one peak component with BE at 103.7 eV, [40–42]. No obvious spectrum of C 1s was observed, indicating that the silica had not been modified or contaminated.

Table 1
Preparation condition and typical properties of the adsorbents.

No.	Average pore size (nm)	Pore volume (cm^3/g)	BET surface area (m^2/g)	Absorbed dose (kGy)	GY (%)	IEC (mmol/g)	Cr(VI) uptake (mg/g)
I-1	15.5	1.18	303.8	40	17.6	0.91	55
I-2				60	20.7	1.03	58
II-1	29.2	1.23	169.1	40	13.8	0.73	43
II-2				60	14.3	0.74	45
III-1	9.5	0.92	388.7	40	23.5	1.14	65
III-2				60	28.2	1.30	68

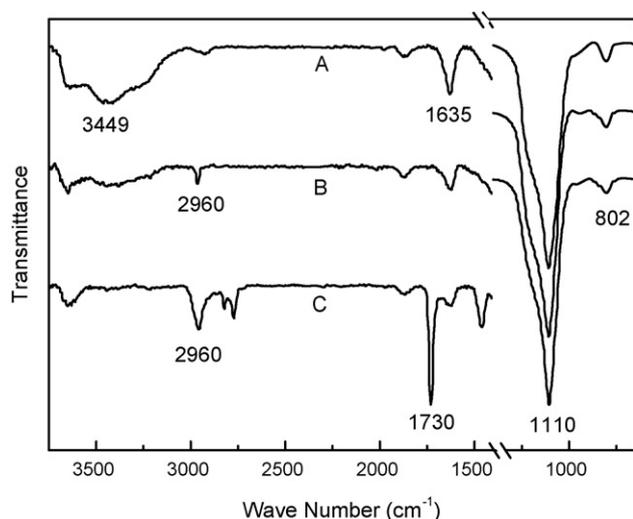


Fig. 3. FTIR spectra of the original silica (A), silanized silica (B) and DMAEMA grafted silica (C).

Fig. 4(B1 and B2) shows the Si 1s and C 1s core-level spectra of the silanized silica, respectively. The C 1s core-level spectrum could be curve-fitted with two peak components with BEs at about 284.8 and 286.3 eV, attributing to the CH₃ and C–O species, respectively. Moreover, the Si 1s core-level spectrum could also be curve-fitted with two peak components with BEs at 101.5 and 103.8 eV, which could be attributed to Si–O–C and Si–O₂ species, respectively. From the Si 1s and C 1s spectra, it could be concluded that the function groups of the silanization agent were introduced into the silica matrix, i.e. trimethylchlorosilane has reacted with silica hydroxyl group according to the reaction route as shown in Fig. 1.

Fig. 4(C1 and C2) exhibits the N 1s and C 1s core-level spectra of the DMAEMA grafted silica. The C 1s core-level spectrum could be curve-fitted with three components with BEs at about 284.8,

286.2 and 288.7 eV that could be attributed to CH₃, C–O and C=O species, respectively. The appearance of C=O at 288.7 eV proved that DMAEMA have been grafted onto the silica. Furthermore, the N 1s core-level spectrum could be curve-fitted with two peak components with BEs at about 399.4 and 401.9 eV, owing to –N(CH₃)₂ and –NH⁺(CH₃)₂Cl[–] species, respectively [24,43], which certified that the grafting process has been performed as designed.

3.1.4. Ion exchange capacity (IEC)

As shown in Table 1, the IEC of the adsorbent was very high and increased with GY. Moreover, the Cr(VI) uptake was also increased with IEC because the higher IEC reflected that there were more amino groups on the silica surface. The Cr(VI) uptake increased from 43 to 68 mg/g, while the IEC of the adsorbents increased from 0.73 to 1.30 mmol/g. Therefore, the III-2 adsorbent with the highest IEC and the highest Cr(VI) uptake was used for the following adsorption experiment.

3.2. Absorption of Cr(VI)

3.2.1. The adsorption kinetics

The time to reach saturated adsorption is of great importance for evaluating the affinity of the adsorbent to the Cr(VI) ions. Therefore, the effect of the stirring time on the adsorption of Cr(VI) at room temperature was studied (Fig. 5). Obviously, there was a burst adsorption step within a contact time of about 15 min and then leveled off. The results indicated the adsorbent had rather rapid adsorption kinetics and a contact time of 40 min was sufficient for the adsorption of Cr(VI) using this adsorbent.

3.2.2. Effect of adsorbent feed

The adsorbent feed is another important parameter because it has direct relation to the capacity of an adsorbent for a given initial concentration at the operating conditions. The effect of the adsorbent feed on the sorption of Cr(VI) was shown in Fig. 6. As the adsorbent feed increased from 0.1 to 1.0 g/L, the recovery of

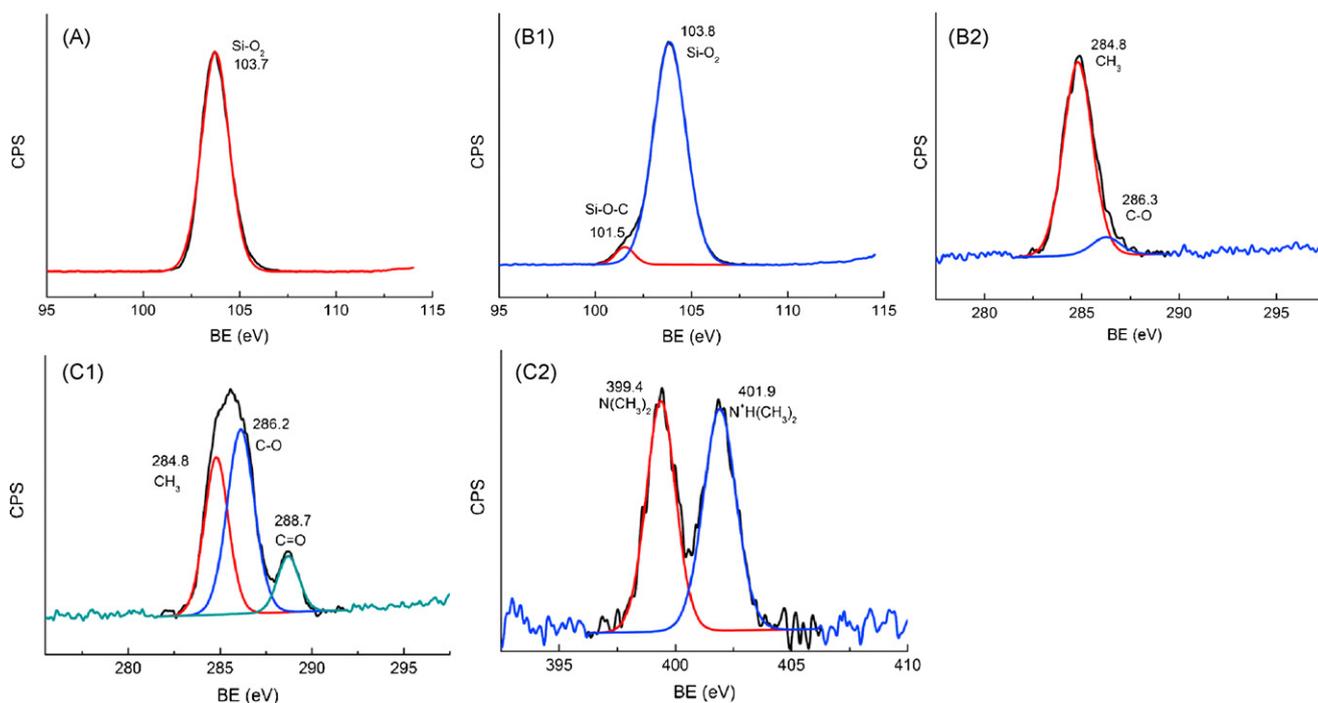


Fig. 4. XPS spectra of the samples: Si 1s peak of original silica (A); Si 2p and C 1s peaks of silanized silica (B1 and B2); C 1s and N 1s peaks of DMAEMA grafted silica (C1 and C2).

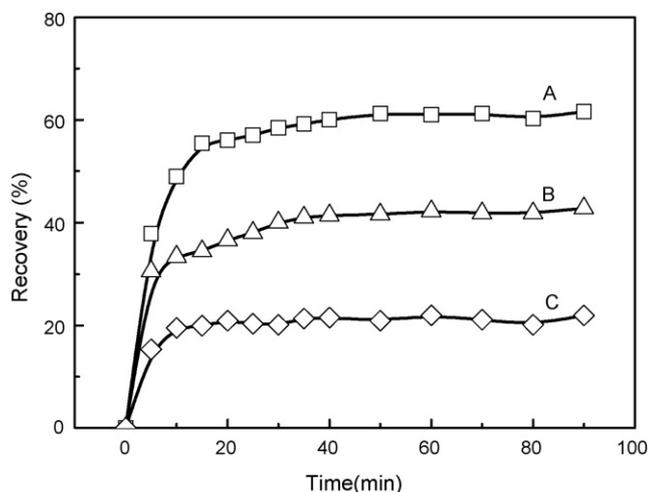


Fig. 5. Effect of the contact time on the adsorption kinetics of Cr(VI) in 50 mL 100 mg/L solutions. (Adsorbent feed: 1.0 g/L (A), 0.6 g/L (B), 0.2 g/L (C); pH: 5.0).

Cr(VI) increased from 21.9% to about 79.3% accordingly. Besides, the increase in the recovery of Cr(VI) was attributed to the increase of the absolute adsorption surface.

3.2.3. Effect of pH

The effect of pH on the Cr(VI) uptake was showed in Fig. 7. It could be seen that the adsorbent had a wide working pH range. While the pH increased from 0.4 to 2.5, the Cr(VI) uptake increased from 32 to 68 mg/g. In the pH range of 2.5 to 5.0, the Cr(VI) uptake maintained a stable value of ca. 68 mg/g. In addition, the Cr(VI) uptake decreased with pH when the pH value was in the range of 7.0–11.0. However, even when the pH reached 11.0, the adsorbents still showed a sound Cr(VI) uptake of 30 mg/g. Thus, it could be concluded that the optimal application condition of the adsorbent was in the pH range of 2.5 to 5.0. In addition, the adsorbent performed a considerable uptake of Cr(VI) even at strong acidic, the Cr(VI) uptake at 4 mol/L HNO₃ was determined to be 22 mg/g. Weng et al. [11] have summarized the maximal uptake of Cr(VI) adsorbents, which was ranging from 0.15 to 256 mg/g [8,11,14,33]. Comparing with these values, the adsorbent prepared in this work was in a medium level. Likewise, the high acidic and alkaline resistant of the adsorbent provided the new adsorbent a far-ranging applied space and applied outlook, especially in some extreme environment.

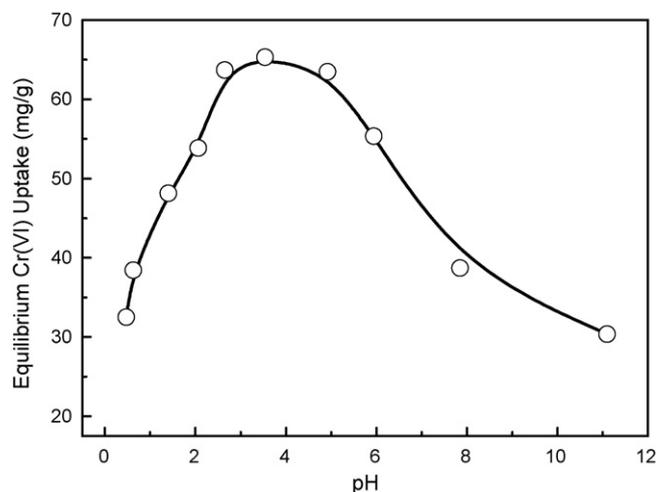


Fig. 7. Effect of pH on Cr(VI) uptake of the adsorbent (Cr(VI) concentration: 100 mg/L; adsorbent feed: 1.0 g/L; stirring time: 40 min; V: 50 mL).

Cr(VI) can exist in several stable forms such as Cr₂O₇²⁻, HCrO₄⁻, H₂Cr₂O₇ and CrO₄²⁻, and the relative abundance of them mainly depends on the pH of the solution and Cr(VI) concentration. H₂CrO₄ exists mainly at pH less than about 1.0; HCrO₄⁻ predominates in the pH range of 1.0–6.0; and when the pH increases to above 7.0, CrO₄²⁻ will be the primary form [8]. So when the pH is changed, the existed form of Cr(VI) will influence the Cr(VI) uptake. On the other hand, when pH is less than 7.0, tertiary-ammonium group of PDMAEMA grafted silica was protonated, so the structure of adsorbent also influences the Cr(VI) uptake after changing pH. In this work, we found that the Cr(VI) uptake maintained a high value in the pH range of 2.5–5.0, which is attributed mainly to electrostatic attraction between the HCrO₄⁻ ions and the adsorbent. However, when the pH is reduced to less than 1.0, electrostatic interaction will be reduced as Cr(VI) mainly exists in the form of H₂Cr₂O₇. At pH higher than 7.0, OH⁻ competes with the Cr(VI) ions and deprotonation processes occur in the adsorbent, resulting in the decrease of Cr(VI) uptake. Other kinds of adsorbents with amino functional groups have been reported in literature. The results have also shown that the adsorption at the pH range of 1.0–6.0 can be mainly attributed to the electrostatic attraction, while at higher or lower pH, the chelation interaction, hydrogen bonding and the weak van der Waals forces could be responsible for the adsorption [25,26,44–47].

3.2.4. Adsorption isotherm

The Langmuir isotherm model was applied to establish the relationship between the amount of Cr(VI) uptake and their equilibrium concentration in aqueous solution. The experimental data was fitted with the linear form of the Langmuir equation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (4)$$

where C_e is the equilibrium concentration of Cr(VI) (mg/L) and q_e is the amount of Cr(VI) adsorbed by per gram adsorbent (mg/g). q_m and K_L are Langmuir constant related to the adsorption capacity (mg/g) and the adsorption energy (L/g), respectively. q_m and K_L were obtained from the slope and the intercept of the linear line of C_e/q_e versus C_e , respectively.

The Langmuir plot for Cr(VI) adsorption using the adsorbent is shown in Fig. 8. The results revealed that the adsorption well fitted the linear Langmuir model. From the linear fit of the plot, the isotherm constants q_m and K_L could be calculated as 87.5 mg/g and 0.024 L/g, respectively. The linear relation coefficient r was also calculated. The high value of r (0.992) indicated the applicability of the Langmuir isotherm model for the adsorption of Cr(VI) by the adsor-

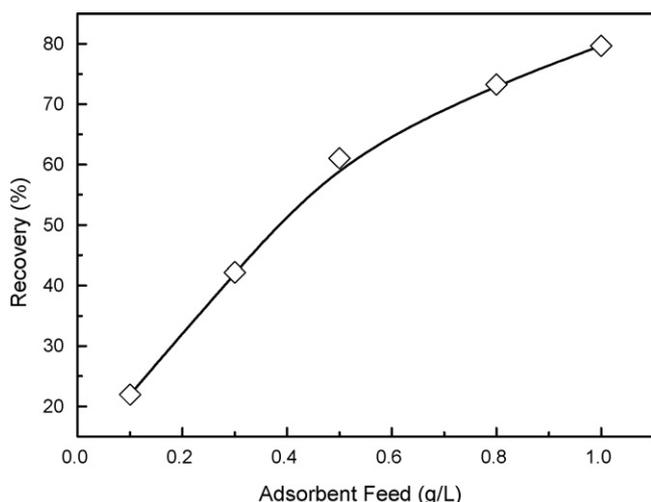


Fig. 6. Effect of the adsorbent feed on the adsorption of Cr(VI) (Cr(VI) concentration: 100 mg/L; stirring time: 40 min; pH: 5.0; V: 50 mL).

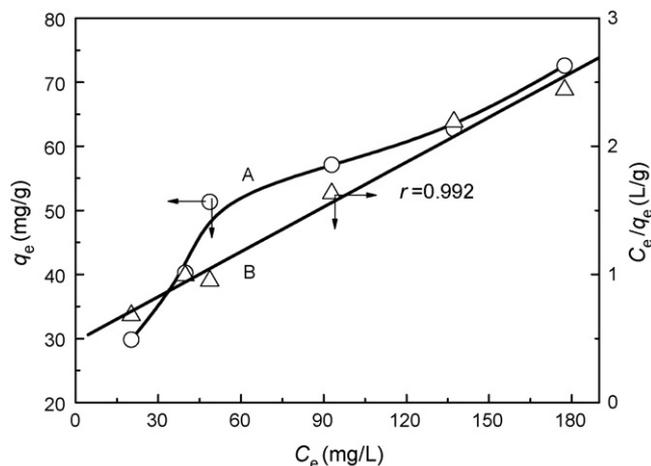


Fig. 8. Experimental Cr(VI) adsorption on the adsorbent (A) and Langmuir linear plot (B). (Adsorbent feed: 1.0 g/L; stirring time: 40 min; pH: 5.0; V: 50 mL).

bent prepared in this work. Nevertheless the theoretical maximum adsorption capacity was higher than the experimental data, it is common when compared with other works [13,14], and might be explained by the incomplete contact of Cr(VI) and the adsorbent.

4. Conclusion

Using γ -ray-induced grafting technique, a convenient fabrication method of adsorbent, was developed and the subsequent characteristics showed that the prepared adsorbent had a high IEC (ca. 1.3 mmol/g) and a high Cr(VI) uptake (ca. 68 mg/g) in the pH range of 2.5–5.0. Even in extreme conditions such as in strong acidic (4.0 mol/L HNO₃) or alkaline (pH 11.0) solutions, the adsorbent still had a considerable Cr(VI) uptake of ca. 22 and 30 mg/g, respectively. The adsorption isotherm was investigated, revealing that the adsorption was fitted with the Langmuir model. As a consequence, there is no denying that the work has provided a new candidate of adsorbent for removing heavy-metal-ions like Cr(VI) ions from waste waters.

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